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IMMOBILIZATION OF AM-241, FORMED UNDER PLUTONIUM METAL CONVERSION, INTO MONAZITE-TYPE CERAMICS

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ABSTRACT

Lanthanum orthophosphate with the monazite structure was proposed on examinations as a suitable matrix for immobilization of future americium-containing liquid wastes, which could be formed in conversion of metallic plutonium into oxide at PA "Mayak."

Specimens of monazite non-active ceramics were fabricated from $LaPO_4$ powders obtained using a thin-film evaporator by either hot-pressing or cold-pressing and sintering at 900–1300 °C. According to electron microprobe analysis (EMPA), scanning electron microscopy (SEM), and X-ray diffraction (XRD), which were used for characterization of produced samples, all specimens did not contain any phase other than the monoclinic monazite phase. Ceramics having the specific activity of Am-241 $2.13 \cdot 10^7$ Bq/g were prepared by only cold-pressing with subsequent sintering at 1300°C during 1 hour. The normalized leach rates of lanthanum and americium in distilled water at 90°C were less than $1.2 \cdot 10^{-4}$ and $2.3\ 10^{-4}$ $g/m^2 \cdot$day, respectively.

INTRODUCTION

PA "Mayak" in Russia was created in the late 1940's to produce weapon-grade plutonium with the aim of reaching nuclear weapon parity.

At the present time, due to great changes in the world and the necessity of nonproliferation disposition of excess plutonium, PA "Mayak" will be assigned the new mission of plutonium-metal-to-oxide conversion process.

This process will generate highly active liquid americium-241 waste streams, containing small amounts of impurities such as Si, Al, Gd, and others. It is well known [1–3] that lanthanide orthophosphates with monazite structure are very promising matrix for immobilization of actinides. The major advantages of monazite ceramic waste forms are high waste loadings, chemical durability and radiation stability. The density of monazite ceramic is normally between 4.0 and 5.0 g/cm^3, which significantly reduces the volume of the final product in comparison with borosilicate glass.

Nevertheless, the main commonly used technology of monazite ceramic waste forms fabrication, based on the urea precipitation process, has some disadvantage due to the emission of substantial quantities of ammonia in radiochemical conditions [3].

To improve the process and adapt it to "Mayak" practice, it was decided to use thin–film evaporator (TFE) for lanthanide ceramic precursor powder with a different ratio La_2O_3:P_2O_5 production. The resulting fine powders were used without milling, mixing, plasticizer addition, and lubrication to produce high-density monazite ceramic specimens by both hot-pressing and cold-pressing and by following with sintering.

SYNTHESIS AND PROPERTIES OF SINGLE-PHASE MONAZITE CERAMICS.

The single-phase monazite ceramics were produced by the hot-pressing method of lanthanum orthophosphate powders obtained with a thin-film evaporator (TFE). Synthesis of monazite ceramics was performed in accordance with two variants, which are presented in Fig.1.

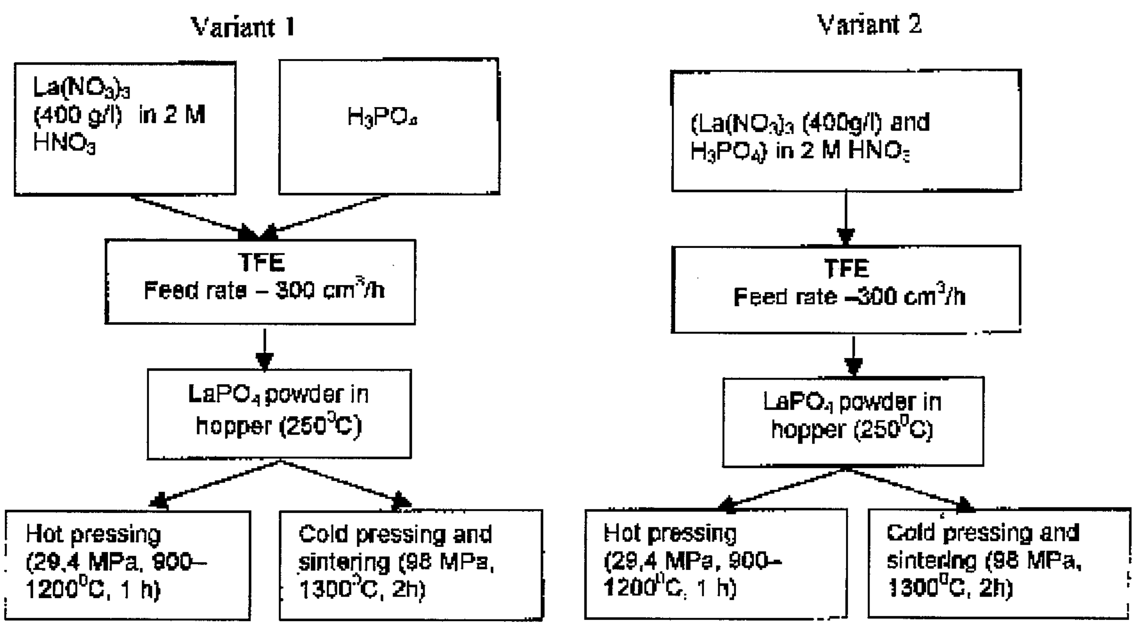

Fig.1. Schemes of synthesis of monazite ceramics

It is necessary to keep the exact ratio of the initial solutions of lanthanum nitrate and orthophosphoric acid to form of lanthanum orthophosphate if the process is conducted according to the variant 1. By contrast, in variant 2 it is not necessary because the initial solutions were previously mixed, and the stable colloidal solution was fed to TFE.

The powder layer formed on the heat-exchanger surface was removed by rotor blades and was collected in the hopper heated at 250°C. To improve TFE operation, the small amount of stripper (polyacrylamide) was added in the initial solution. It was determined by XRD that the powder obtained represented $LaPO_4$ with the monazite structure and contained an amorphous phase.

Pellets with the weight of ~10 g and diameter of 20 mm were formed from the powder by hot-pressing in a graphite mold at 29.4 MPa pressure and at temperature 900–1200°C. Pressing temperature and some properties of the pellets are presented in Table I.

Table I. Pressing temperature and some properties of $LaPO_4$ pellets

№	Pressing temperature, °C	Apparent density, g/cm³	% of the theoretical density	Open porosity, % vol.
1	900	4.24	83.0	9.8
2*	1000	4.90	96.0	1.0
3	1000	4.90	96.0	<0.1
4	1100	4.90	96.0	<0.1
5*	1150	4.67	91.0	<0.1
6	1200	5.00	97.6	<0.1
7	1200	4.93	96.0	<0.1

*Samples were prepared without stripper additive

As can be seen from Table I, dense and low-porosity ceramics are formed at relatively moderate temperature (1000°C). On the XRD data, monazite crystallites have been enlarged from 50 nm (at 250°C) to >100 nm, and the amorphous phase has been crystallized during hot-pressing. As a result, single-phase ceramics are formed. The uniformity and chemical composition ($LaPO_4$) of monazite ceramics were confirmed by EMPA, SEM, and XRD.

SEM photomicrographs of ceramic samples #2 and 3 (Fig. 2 and 3), prepared under similar conditions with addition of stripper and without, demonstrated the stripper influence on the quality of the ceramics.

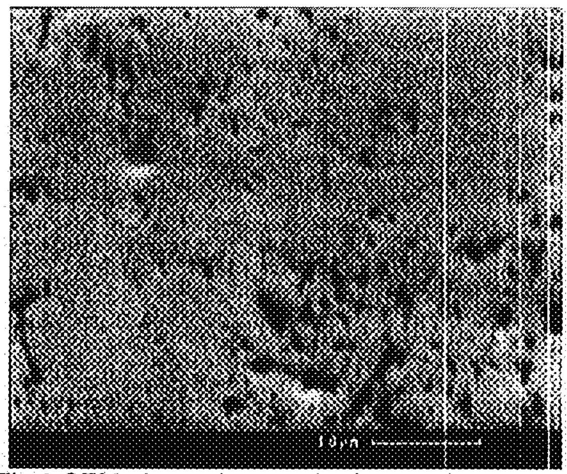

Fig 2.SEM photomicrograph of monazite ceramic (# 2), without stripper additive

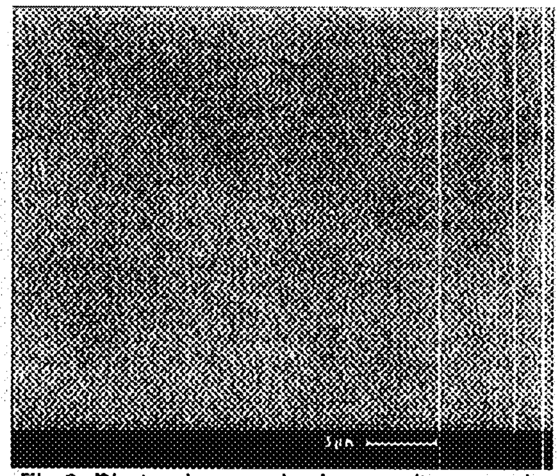

Fig 3. Photomicrograph of monazite ceramic (# 3), with stripper additive

As seen from Figs. 2 and 3, the addition of stripper improves the ceramic quality owing to formation of more fine-dispersive powder.

Two-phase ceramic is formed at more than 5 mol% excess of orthophosphoric acid. The phase compositions of ceramics prepared under similar conditions with different molar ratio La_2O_3:P_2O_5 are shown in Table II.

Table II. Phase compositions of ceramics with different molar ratio La_2O_3:P_2O_5

Molar ratio	Phase compositions
1 : 1	$LaPO_4$ (monazite)
1: 1.05	$LaPO_4$ (monazite)
1 : 1.1	$LaPO_4$ (monazite)+ LaP_3O_9
1 : 1.3	$LaPO_4$ (monazite) +LaP_3O_9

A 10–30 mol % orthophosphoric acid excess results in $LaPO_4$ (monazite) and LaP_3O_9. The SEM photomicrograph of the two-phase ceramics is shown in Fig. 4.

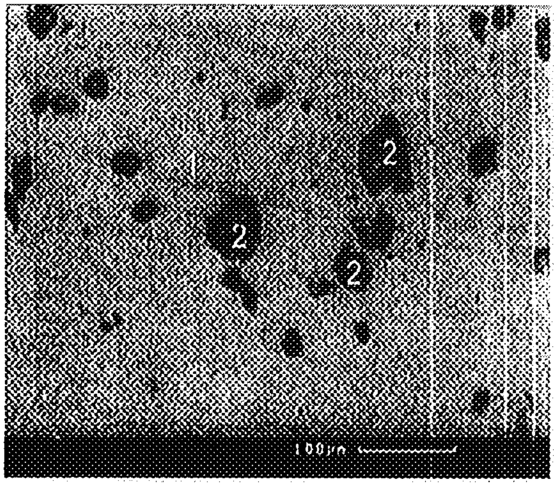

Fig 4. SEM photomicrograph of two-phase monazite ceramics: (1) $LaPO_4$; (2) LaP_3O_9.

MONAZITE CERAMICS DOPED WITH AMERICIUM-241

Two ceramic samples were sintered under similar conditions by cold axial pressing (98 MPa) with following sintering at 1300°C during 2 hours. One of them was doped by Am-241. To prepare the $LaPO_4$ powder, a mixture of $La(NO_3)_3$ solution in 1 M HNO_3 and H_3PO_4 having 5 mol% excess was evaporated to dryness. $Am(NO_3)_3$ solution in 1 M HNO_3 was added to a $La(NO_3)_3$ solution in 1 M HNO_3 to obtain the doped sample. The resulting powder was heated at 700°C and ground before pressing. The apparent densities of the samples—that is, 4.3 g/cm^3 —were 84% of the calculated value.

Only an undoped sample was studied by EMPA and XRD. These methods showed that the undoped sample contains only one monazite phase. It can be assumed that the doped sample has the same composition because synthesis conditions were identical.

CHEMICAL STABILITY

The leaching properties of the fabricated waste forms were investigated by conducting the MCC-1 test [4]. The leaching conditions were as follows: leachant; distilled water; leach test vessel material; teflon; $S/V=10\text{м}^{-1}$; leach test temperature 90°C; the leach test was run for 7 days.
The following ceramic samples were tested:

- Sample #3 – hot-pressed at 1000°C (Table I)
- Sample #6 – hot-pressed at 1200°C (Table I)
- Cold-pressed sample – 98 Mpa, with sintering at 1300°C during 2 hours.

The leachates were analyzed by atomic emission spectroscopy with inductively coupled plasma. The results of the leaching tests are summarized in Table III.

Table III. Results of the MCC-1 test

Sample	Concentration La, mg/l
#3	<0.005
#6	<0.005
Cold-pressing	<0.005

The concentrations of lanthanum in the leachate were below detection level (0.005 mg/l) in all tests. The values of lanthanum normalized release rates, which were calculated from these concentrations and obviously overestimated, are less than $1.2\cdot10^{-4}$ g/m^2/day and testify to high chemical stability of ceramics.

The ceramics doped with americium were also tested by the MCC-1 (Table IV). The americium-241 content was determined by gamma spectrometry. Specific activity of Am-241 in the ceramic was $2.13\cdot10^7$ Bq/g.

Table IV. Normalized leach rate of Am-241 from the $LaPO_4$ monazite ceramic sample

Sample activity, Bq	Leachate specific	Normalized leach rate,

	activity, Bq/ml	$g/m^2 \cdot day$
$1.48 \cdot 10^7$	0.35±0.10	$2.34 \cdot 10^{-4}$

As can be seen from Table IV, the normalized leach rate of Am-241 from the studied sample is low enough and correlates with the data for synthetic monazite [1].

CONCLUSIONS

1. The principal possibility of TFE using for $LaPO_4$ powder production was shown.
2. Addition of polyacrylamide in the amount of 1 wt% of lanthanum orthophosphate calculated weight improves the TFE operation parameters and quality of the ceramic obtained.
3. Dense low-porosity monazite ceramics (apparent density averages of 96% of the calculated value) can be prepared by hot-pressing at temperature 1000°C.
4. The XRD, EMPA, and SEM showed that the samples are uniform and consist of $LaPO_4$ with monazite structure. At excess H_3PO_4 more as 5-mol% additional phase LaP_3O_9 is formed along with monazite.
5. The ceramic has high chemical stability; the normalized rates of lanthanum and americium losses are as low as ~10^{-4} $g/m^2 \cdot day$ and are comparable with those for synthetic monazites

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